

QUALITY ASSURANCE PROJECT PLAN
Category I Research Project

**Fate, Transport, and Characterization of Contaminants in Hydraulic
Fracturing Water in Wastewater Treatment Processes**

EPA QA Log Number: W-18974

U.S. Environmental Protection Agency
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Revision 0
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SECTION A - PROJECT MANAGEMENT

A1 TITLE APPROVAL SHEET

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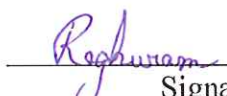
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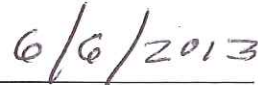

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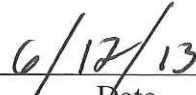


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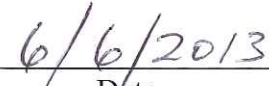


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Disclaimer

EPA does not consider this internal planning document an official Agency dissemination of information under the Agency's Information Quality Guidelines, because it is not being used to formulate or support a regulation or guidance; or to represent a final Agency decision or position. This planning document describes the overall quality assurance approach that will be used during the research study. Mention of trade names or commercial products in this planning document does not constitute endorsement or recommendation for use.

The EPA Quality System and the HF Research Study

EPA requires that all data collected for the characterization of environmental processes and conditions are of the appropriate type and quality for their intended use. This is accomplished through an Agency-wide quality system for environmental data. Components of the EPA quality system can be found at <http://www.epa.gov/quality/>. EPA policy is based on the national consensus standard ANSI/ASQ E4-2004 *Quality Systems for Environmental Data and Technology Programs: Requirements with Guidance for Use*. This standard recommends a tiered approach that includes the development and use of Quality Management Plans (QMPs). The organizational units in EPA that generate and/or use environmental data are required to have Agency-approved QMPs. Programmatic QMPs are also written when program managers and their QA staff decide a program is of sufficient complexity to benefit from a QMP, as was done for the study of the potential impacts of hydraulic fracturing (HF) on drinking water resources. The HF QMP describes the program's organizational structure, defines and assigns quality assurance (QA) and quality control (QC) responsibilities, and describes the processes and procedures used to plan, implement and assess the effectiveness of the quality system. The HF QMP is then supported by project-specific QA project plans (QAPPs). The QAPPs provide the technical details and associated QA/QC procedures for the research projects that address questions posed by EPA about the HF water cycle and as described in the *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (EPA/600/R-11/122/November 2011/[www.epa.gov/hydraulic fracturing](http://www.epa.gov/hydraulic%20fracturing)). The results of the research projects will provide the foundation for EPA's 2014 study report.

This QAPP provides information concerning the Wastewater Treatment and Waste Disposal Stage Projects of the HF water cycle as found in Figure 1 of the HF QMP and as described in the HF Study Plan. Appendix A of the HF QMP includes the links between the HF Study Plan questions and those QAPPs available at the time the HF QMP was published.

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A2.1 ACRONYMS/DEFINITIONS

ADQ	Audit of Data Quality
ASQ	American Society for Quality
AWBERC	Andrew W. Breidenbach Environmental Research Center
CQA	Certified Quality Auditor
CQE	Certified Quality Engineer
DI	Deionized
EPA	U.S. Environmental Protection Agency
HF	Hydraulic Fracturing
LFB	Laboratory Fortified Blank
MDL	Method Detection Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NH ₃	Ammonia
NO ₃	Nitrate
NOM	Natural Organic Material
NRMRL	National Risk Management Research Laboratory
OGWW	Treatment of water from oil and gas exploration activities
ORD	Office of Research and Development
PE	Professional Engineer
Pegasus	Pegasus Technical Services, Inc.
PI	Principal Investigator
POTW	Publicly Owned Treatment Works
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
QMP	Quality Management Plan
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
Shaw	Shaw Environmental & Infrastructure, Inc.
SHEM	Safety, Health, and Environmental Management
SOP	Standard Operating Procedure
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
T&E	Test and Evaluation
TSA	Technical System Assessment
TSS	Total Suspended Solids
UC	University of Cincinnati
VSS	Volatile Suspended Solids
WA	Work Assignment
WSWRD	Water Supply and Water Resources Division
WW	Wastewater

A3 DISTRIBUTION LIST

U.S. Environmental Protection Agency

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Steven Jones, ASQ CQA/CQE	Contract Quality Assurance Manager
George Sorial, Ph.D.	University of Cincinnati Manager
Pablo Campo-Moreno, Ph.D.	Work Assignment Leader
Shahram Ghasemzadeh	WA Staff

A4 PROJECT/TASK ORGANIZATION

The overall project management and distribution of responsibilities among the project personnel are described in this section. Figure A5-1 shows the project organization chart and Table A5-1 presents the project roles and responsibilities of the various project staff.

Dr. Christopher A. Impellitteri, U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD)/National Risk Management Research Laboratory (NRMRL)/Water Supply and Water Resources Division (WSWRD) at the EPA the Andrew W. Breidenbach Environmental Research Center (AWBERC) is the principal investigator (PI) of the project. Dr. Impellitteri is responsible for planning and coordination of field sample collection, transportation, processing and preservation, storage, distribution, preparation, analyses, data analyses and final report preparation. Dr. Impellitteri will also serve as Technical Research Lead and liaise with other parties including the Office of Water and utilities in EPA Region 3.

Mr. Craig L. Patterson, P.E., EPA ORD/NRMRL/WSWRD at the EPA Test and Evaluation (T&E) Facility is the EPA Work Assignment (WA) Manager of the project. Mr. Patterson is responsible for overall technical direction of Work Assignment (WA) 2-64 under EPA Contract EP-C-11-006 and ensuring that the data deliverables received from Pegasus Technical Services, Inc. (Pegasus) satisfies the project objectives.

Mr. Kit Daniels, EPA ORD/NRMRL/WSWRD at EPA AWBERC serves as the EPA Project Scientist. Mr. Daniels is responsible for collection, preservation, transportation, processing and distribution of field samples. He is also responsible for maintaining a chain of custody form for the samples. Mr. Daniels may also deliver samples to UC at the direction of the EPA WA Manager or the PI.

Dr. Samuel Hayes, EPA ORD/NRMRL/WSWRD at the EPA AWBERC in Cincinnati, Ohio serves at the WSWRD Associate Division Director.

Dr. John Olszewski, EPA ORD/NRMRL/WSWRD at EPA AWBERC serves as the EPA WSWRD Quality Assurance (QA) Manager with the responsibility for QA review of this Quality Assurance Project Plan (QAPP), conducting QA assessments, and QA review of all deliverables.

Ms. Holly Ferguson, EPA ORD/NRMRL at EPA AWBERC serves as the NRMRL Environmental Technology Assessment, Verification and Outcomes QA Manager and is responsible for QA review of the QAPP, conducting QA assessments, and QA review of the final report.

Mr. Stephen Wright, EPA at the AWBERC in Cincinnati, Ohio serves as the Project Officer for EPA Contract No: EP-C-11-006 under which this QAPP is being written.

Dr. Karen Koran, with Pegasus serves as the Pegasus Project Manager for the Pegasus Contract and is responsible for overall management of Pegasus Contract activities conducted by Pegasus and Pegasus subcontractors.

Dr. Raghuraman Venkatapathy, with Pegasus serves as the Pegasus On-Site Technical

Manager for the Pegasus Contract and is responsible for management of the Pegasus On-Site Program and supervision of On-Site Pegasus Team Staff. In addition, Dr. Venkatapathy oversees the research support work activities conducted at the University of Cincinnati under WA 2-64, and is the primary Pegasus point of contact for all WA 2-64 samples that are shipped/delivered to EPA AWWERC for sample processing. Dr. Venkatapathy is also responsible for ensuring that this QAPP and WA 2-64 deliverables receive an internal full, independent management review, and ensuring that review comments are adequately addressed prior to final delivery or use of the document, and ensuring that environmental data generated under WA 2-64 are performed in accordance with this QAPP.

Dr. George Sorial, with the University of Cincinnati (UC), a subcontractor to Pegasus, serves as the UC Manager and is responsible for overall UC project management, program coordination, and management review of UC deliverables to EPA. The UC Manager is also responsible for maintaining training records for the UC staff, including initial demonstration of analyst proficiency documentation.

Mr. Steven Jones, ASQ CQA/CQE, with Shaw Environmental & Infrastructure, Inc. (Shaw), a subcontractor to Pegasus, serves as the Contract QA Manager for the Pegasus Contract and is responsible for oversight of the Pegasus Quality Management Plan (QMP) quality program implementation, including QA review of documents and deliverables, providing guidance for and verifying implementation of quality program requirements as described in this QAPP, and conducting project assessments. Mr. Jones reports to the Pegasus President and CEO and is organizationally independent of the project.

Dr. Pablo Campo-Moreno with UC serves as the WA Leader for this Pegasus WA and is responsible for project planning and coordination of day-to-day activities that are conducted by the UC staff, and overseeing the activities conducted by the UC staff to ensure implementation of the requirements as stated in this QAPP. Dr. Campo-Moreno is the primary point of contact for all WA 2-64 samples that are shipped/delivered to UC for sample processing/analysis. The WA Leader is also responsible for coordinating the submittal of deliverables to the UC Manager, Pegasus On-Site Technical Manager, and Pegasus Contract QA Manager for review, ensuring that the UC staff received training on the requirements of this QAPP, maintaining project records, including chain of custody forms for received samples, sample analysis, verifying that data generated by the UC staff meet the requirements of this QAPP, data reporting, and ensuring that deliverables are peer reviewed prior to submittal to EPA.

Mr. Shahram Ghasemzadeh, with UC (graduate student) will provide support for this WA. Mr. Ghasemzadeh will be responsible for assisting the WA Leader with the design and maintenance of the experiments as well as chemical analysis.

Figure A4.1 Project Organization

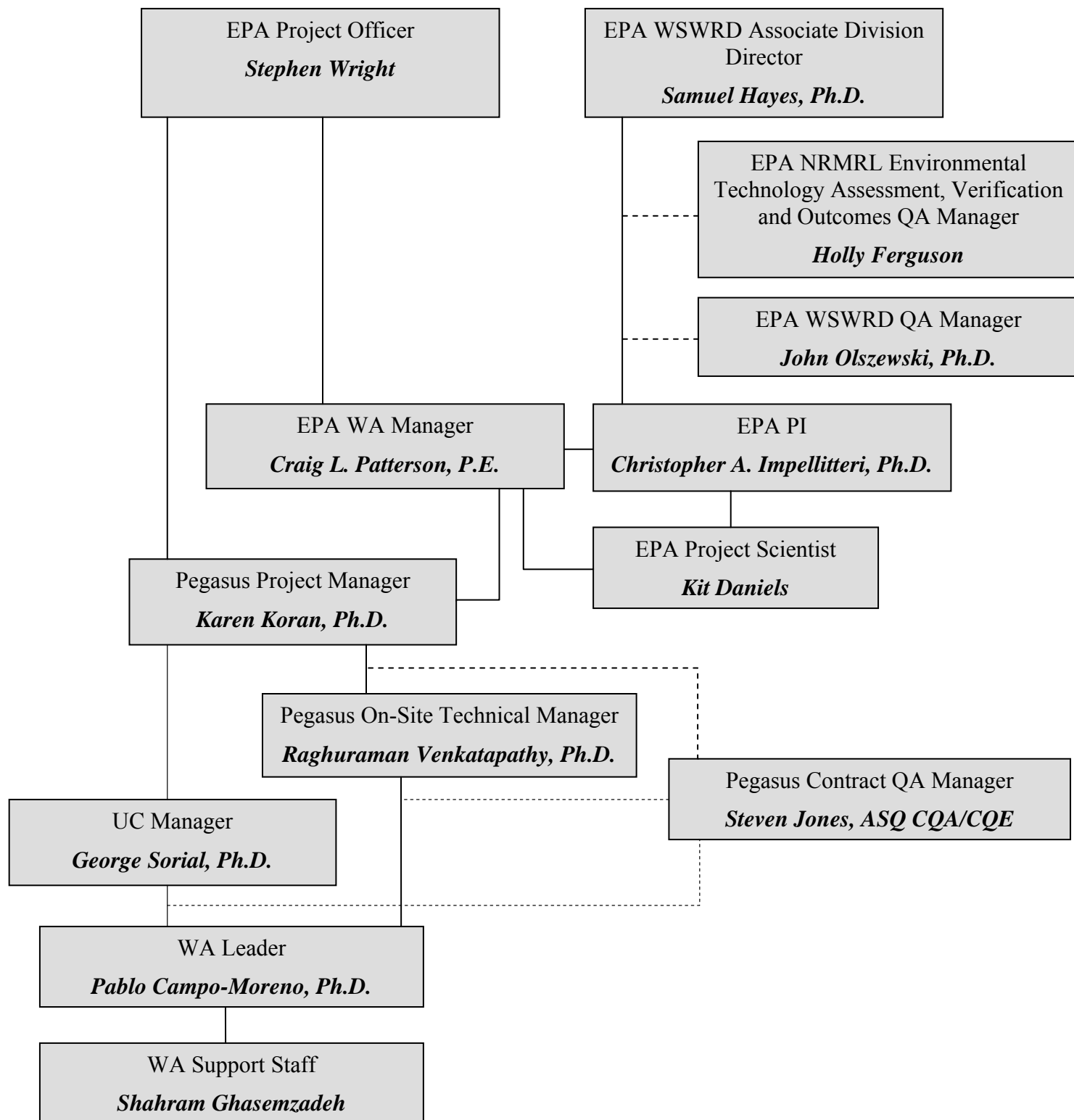


Table A4.1 Project Roles and Contact Information

Name of Person/Affiliation	Project Role	Phone Number, email
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Shahram Ghasemzadeh, Pegasus Subcontractor (UC)	WA Support Staff	(513) 556-3640, ghasemsm@mail.uc.edu

A5 PROBLEM DEFINITION/BACKGROUND

Hydraulic fracturing (hydro-fracking, HF) is widely used to extract oil, shale gas and coal bed methane. This practice for oil and gas exploration causes major challenges for water consumption and management because it consumes a large volume of fresh water and generates the largest single stream of contaminated flow-back wastewater. Hence, the success of the HF technique is dependent on an efficient and cost-effective flow-back wastewater (WW) treatment technology.

This flow-back water typically contains high levels of dissolved solids (including chloride and bromide salts), heavy metals, and hydrocarbons from natural sources as well as chemical additives from various stages of the HF process. In general, treatment of water from oil and gas exploration activities (hereafter referred to as OGWW) has occurred through either admixture to normal wastewater inputs or post-treated wastewater. However, to date, the impacts of such inputs, and in particular, the effects of high total dissolved solids (TDS) levels on secondary wastewater treatment have not been ascertained. The elevated TDS levels are of particular concern because conventional wastewater treatment is generally not effective at their removal.

OGWW may be treated to varying degrees by conventional processes (via publicly owned treatment works [POTWs]) and commercial facilities. Conventional WW treatment is generally a non-chemical natural process using primary settling, aeration basin/activated sludge, and secondary settling tanks. Commercial treatment methods include several chemical and non-chemical methods (i.e., chemical precipitation, adsorption, ion-exchange, advanced oxidation, coagulation/flocculation, thermal, and filtration). The level of contaminants in re-use OGWW, thus, can vary depending on the treatment processes and needs to be evaluated.

Many states and municipalities are still grappling with issues surrounding OGWW treatment because there are concerns about the treatability of OGWW. Some contaminants, such as salts comprising TDS, are not removed by conventional treatment processes and may increase TDS levels in receiving waters. Commercial facilities typically remove TDS (and other contaminants) via an evaporative/distillation processes. Water re-use technologies are widely employed in the Marcellus Shale region in order to treat OGWW on-site to a degree which allows the treated water to be re-injected on another job. In any treatment system, there will eventually be a concentrated sludge, brine, or salt-cake with known and unknown contaminants which cannot be treated and must be disposed in a proper manner.

The overall goal of this Work Assignment (WA) is to assess the impact of TDS present in OGWW on the activated sludge process.

1. To assess the impact of high TDS (NaCl is used as a surrogate for TDS) concentrations on the performance of activated sludge by treating a synthetically prepared medium-strength municipal wastewater with increasing amounts of NaCl.
2. To assess the impact of OGWW TDS on the performance of the activated sludge by treating a synthetically prepared wastewater combined with actual OGWWs from different sources.

A6 PROJECT/TASK DESCRIPTION

It is known that the amount and type of TDS in water can influence aqueous chemistry, particularly upon water treatment. This is particularly true with water which has been impacted by wastewater input from a variety of industrial/resource extraction processes. However, the impact of high TDS on secondary wastewater treatment, especially the microbial population, is relatively unknown. In this component of the study, we will evaluate the effect of TDS on the activated sludge process. Initially, the effect of TDS on activated sludge will be studied using synthetic wastewater dosed with varying amounts of TDS. Later, this study will be repeated with synthetic wastewater that is combined with actual OGWWs from various sources. The rationale for using a synthetic wastewater matrix is to have a homogeneous and reliable feed for the project. OGWW from three to five sources in the Marcellus Shale Region of Eastern United States will be used for the second part of this project.

All experiments in this study will be conducted with chemostats, which are continuous flow reactors that allow keeping cultures under constant chemical conditions for long periods; such devices are ideal for conducting studies on the kinetics of biological growth and substrate removal. These bioreactors will be used in this project to simulate an aerobic activated-sludge process without recycle where bacteria are exposed to high TDS values. Biomass collected from the aerobic compartment of a bioreactor located in Rhodes Hall 525 at UC will be used to seed the chemostats used in this project, since the bioreactors are operated with the same synthetic feed, and are hence adapted to the synthetic wastewater matrix.

The first task will consist of determining the extent of microbial adaptation to TDS, i.e., the highest salt (NaCl) concentration that can be achieved in the synthetic wastewater without organic matter respiration being disrupted. In this case, microbes will be exposed to increasing TDS concentrations, while those of the substrates (carbon and nitrogen) remain constant. For this task, two chemostats will treat a synthetic municipal wastewater whose ionic strength (a measure of TDS) will be adjusted with NaCl. For a given TDS concentration, the upset threshold will be a TOC percent removal $\leq 50\%$.

For the second task, different OGWWs will be fed in combination with the synthetic waste in mixing ratios (v/v) that follow the same TDS levels as Task 1, with the final target set at the maximum concentration obtained using NaCl in Task 1. Hence for Task 2, OGWW will be used in place of NaCl to obtain the target TDS levels in the synthetic wastewater. Again, a TOC removal $\leq 50\%$ will determine the treatment's failure. Since OGWWs may vary in TDS composition owing to their different origins, here, the objective will be to gain insight about the effect of different compositions of TDS on activated sludge performance.

The critical parameters for this project are TDS and TOC in the influent and effluents, because these variables will allow us to evaluate the aerobic removal of organic matter under different ionic strengths (TDS concentrations). Additional non-critical parameters include influent and effluent acetic acid as well as TSS/VSS and pH measured in the mixed liquor as these parameters provide information about biomass activity. The concentrations of ammonia (influent and effluents) and nitrite/nitrate (effluents) are considered non-critical as well; these data will help to determine if nitrification is taking place in the systems.

As stated above, this project can be sub-divided into two tasks:

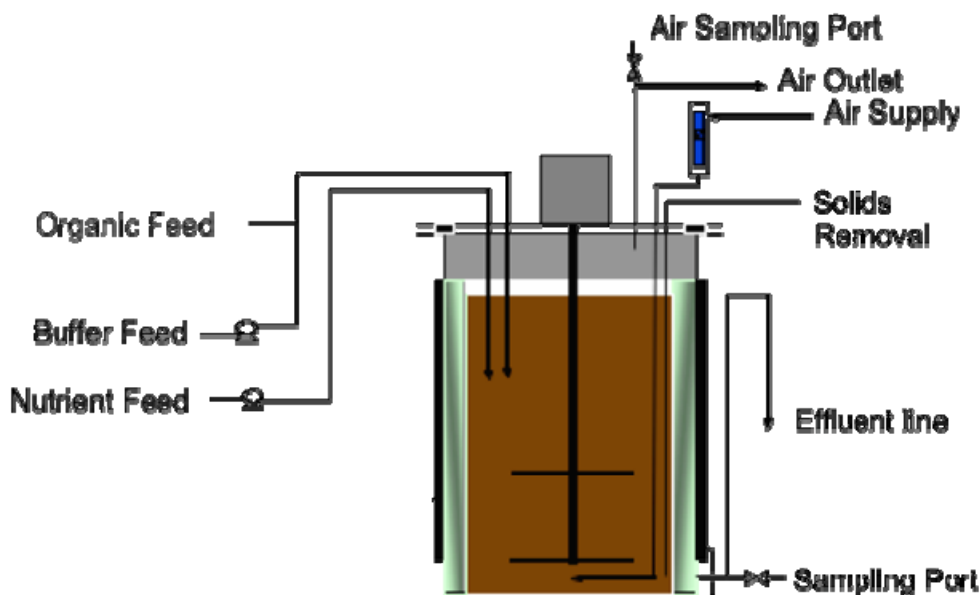
A6.1 Task 1 – Evaluating the effect of total dissolved solids (NaCl) on the activated sludge process using synthetic wastewater.

A6.2 Task 2 – Evaluating the impact of OGWW on the performance of the activated sludge.

A6.1 Task 1 - Evaluating the effect of total dissolved solids on the activated sludge process

Two bench-scale 6-liter porous pot chemostats (Reactors 1 and 2) will be prepared through modification of existing reactors at UC's Engineering Research Center Room 761. Both reactors are made of 304-stainless steel with an internal diameter of 21.6 cm and a height of 30.5 cm (Figure A6.1). Each reactor will contain a 0.48 cm thick filter grade polyethylene porous pot with a mean flow pore size of 18-28 μm for the retention of biomass. The total volume of each reactor is 8 L, while the volume of the mixed liquor within the porous pot will be 6 L. The contents of the porous pot will be kept well-mixed via a magnetically coupled variable speed mixer. Although the reactors can be temperature controlled, they will be run at room temperature (21 ± 2 °C).

Figure A6.1 Schematic of the chemostat reactor.



Synthetic wastewater

A synthetic feed simulating medium-strength municipal wastewater of approximately 200 mg/L Chemical Oxygen Demand (COD) and 40 mg/L total Kjeldahl nitrogen will be prepared in deionized (DI) water. This synthetic wastewater will contain a mixture of proteinaceous matter, carbohydrates, starches, fatty acids, ammonium, phosphates, and several macro- and micro-nutrients needed to support microbial growth. The constituents will be grouped as follows:

- Organics: casein, tryptone, starch, glycerol, and caproic acid.
- Nutrients: ammonium sulfate, magnesium sulfate, calcium chloride, potassium phosphate, cupric sulfate, sodium molybdate, manganese sulfate, zinc chloride, iron chloride, cobalt chloride, and acetic acid.
- Buffer: sodium carbonate.

In order to minimize any degradation of the components prior to entry into the systems, each group will be fed separately from concentrated solutions so that three reservoirs (21-L carboys; one for each group) will be connected to both reactors by separate tubing lines and corresponding peristaltic pumps (3 per reactor). Each line will have a conduit linking the reservoir to a tee where the flow splits into two branches to serve both reactors. For sampling purposes, a quick disconnect-fitting will be located between the reservoir and the tee. Every line will contribute 1/3 to the total influent and will combine inside the chemostats. The final flow rate will be 9 L/day, which results in a hydraulic retention time of 16 h. The detailed composition of the feed inside of the reactor is presented in Table A6.1. All these chemicals will be ACS reagent quality or equivalent. In order to prepare the group solutions in 21 L of DI water, the amount of each component can be calculated by multiplying the concentrations presented in Table A6.1 by 63, this is, the inverse of the influent dilution factor (9/3) times the DI water volume.

Table A6.1 Synthetic wastewater composition in the chemostats

Component	Final Concentration, mg/L	Component	Final Concentration, mg/L
Organics		Ammonium sulfate	116.0
Casein	47.0	Acetic Acid	500.0
Tryptone	47.0	Micronutrients	
Starch	84.4	Cupric sulfate	0.09
Glycerol	12.0	Sodium molybdate	0.15
Caproic acid	11.6	Manganese sulfate	0.13
Macronutrients		Zinc chloride	0.23
		Iron chloride	0.42
Magnesium sulfate	69.6	Cobalt chloride	0.42
Calcium chloride	22.5	Buffer	
Potassium phosphate	27.6	Sodium carbonate	317

Operation of the two chemostats

Both reactors will be operated in parallel at a solids retention time (SRT) of four days (solids shall be wasted at the rate of 1/4 of the mixed liquor volume daily) and will be dosed at the same TDS concentration. With this setup, one reactor will serve as a backup just in case the high TDS levels disrupt one of the systems. In this case, the experiment will be continued with the remaining reactor, thus saving the time necessary to start and stabilize new fresh biomass. The biomass will require a start-up phase to achieve steady state. During this stage, which is defined as 3 consecutive SRTs, only synthetic wastewater without NaCl will be fed into the reactors. Subsequently, the influent TDS concentration will be ramped up by adding NaCl in cumulative doses of 10 g/L every 3 SRTs. The maximum extent of adaptation will be determined as highest TDS concentration achieved without upsetting carbon oxidation, which will be indicated by a TOC removal $\leq 50\%$. Upon disruption, the salt concentration in the influent should be scaled back to the nearest level where microbes degraded, at least, 80% of the TOC. This condition will be kept for 3 SRTs before Task 2 is started. NaCl will be incorporated in the influent via the buffer reservoir.

Twice a week (on Tuesdays and Thursdays), the performance of the reactors will be evaluated by analyzing the following quality variables: influent and effluent TDS, acetic acid, TOC, ammonia-N; effluent nitrate-N; and total and volatile suspended solids in the mixed liquor. In this fashion, a total of 3 sampling events will be conducted during the course of each 3 SRT period: aliquots for every variable to be monitored will be collected from both chemostats and preserved as described in Table B2.2. Additionally, in the last sampling event of the 3 SRT interval, two extra sample aliquots will be gathered per chemostats effluent to determine analytical precision and accuracy of acetic acid, TOC, ammonia-N, and nitrate-N measurements in the corresponding effluents. After analyzing these parameters in triplicate, %RSDs and matrix spike recoveries will be calculated; the obtained values should meet the criteria included in Table B5.1.

Since both reactors will run under the same conditions (i.e., one acting as a redundant system), results from one chemostat will suffice to evaluate the TDS impact on the activated sludge. With this purpose, the data series from the reactor showing more consistent effluent quality will be used for interpretation, whereas outcomes of the second unit will not be considered henceforth. As to gauge consistency, TDS and TOC relative standard deviations for both effluents will be calculated per 3-SRT sampling period and the reactor presenting lower percentages for both parameters overall will be selected.

A6.2 Task 2 – Evaluating the impact of OGWW in the performance of the activated sludge

EPA will provide actual OGWWs from three to five different sources to evaluate their effect on the activated sludge. The actual OGWW samples can either be the final effluent from a wastewater treatment facility (WWTF) where OGWW fluids were processed (low salinity) and/or untreated raw materials obtained from the extraction sites (high salinity). These effluent water samples (hereafter referred to as WWTF effluent) are obtained from the effluent of wastewater treatment plants that have treated OGWW (hereafter referred to as WWTF influent).

The samples will not be preserved in the field, and it is not anticipated that the samples will be analyzed within their respective holding times. Therefore, the analyses values will not be considered representative of field values at any time for this study.

Each OGWW source (both influent and effluent) will be tested separately as described in Section A6.1. Hence, a given volume of OGWW will be incorporated to the synthetic wastewater so that, for Reactor 1, the influent TDS concentration will be 10 g/L. Since OGWWs typically have TDS concentrations greater than 100,000 mg/L, the actual amount of OGWW added to the reactor might be a few milliliters (the actual amount will be calculated based on preliminary assessment of the TDS concentrations in OGWW). The actual HF waste will be added to the buffer reservoir. Simultaneously, Reactor 2 will be run in parallel as a control; in this case, the feed will consist of synthetic wastewater fortified with NaCl to match the influent TDS concentration measured for Reactor 1. For OGWW, changes in influent composition (i.e., TDS increments of 10 g/L) will take place every 3 SRTs. Again, a TOC removal $\leq 50\%$ will determine the failure of the treatment. At that point, the OGWW fraction should be reduced to the nearest ratio where the chemostats oxidized at least 80% of the TOC. This condition will be monitored for 3 SRTs before a different OGWW is tested. In this task, the reactors will share 21-L reservoirs for Organics and Nutrients mixes whereas independent carboys will be required for buffer solutions.

As in Task 1, reactors' performance will be assessed by analyzing, twice a week (on Tuesdays and Thursdays), these quality variables: influent and effluent TDS, acetic acid, TOC, ammonia-N; effluent nitrate-N; and total and volatile suspended solids in the mixed liquor. Hence, a total of 3 sampling events will be conducted during the course of each 3 SRT period. Aliquots for every variable to be monitored will be collected from both chemostats and preserved as described in Table B2.2. Additionally, in the last sampling event of the 3 SRT interval, two extra sample aliquots will be gathered per chemostat to determine analytical precision and accuracy of acetic acid, TOC, ammonia-N, and nitrate-N measurements in the corresponding effluents. After analyzing these parameters in triplicate, %RSDs and matrix spike recoveries will be calculated; the obtained values should meet the criteria included in Table B5.1.

Comparisons between Reactor 1 and Reactor 2 will be conducted to determine the effect of OGWW on carbon oxidation. Hence, acetic acid and TOC removals efficiency from both systems will be compared by Student's *t*-test at 95% confidence for each of the variables. In this case, the null hypothesis will be that fracturing waste does not affect the microbial performance. Additional comparisons between the two reactors will be conducted to determine the effect of OGWW on nitrogen oxidation using ammonia and nitrate-N values as the variables. The results from the nitrogen oxidation analysis will only be used for confirmatory purposes.

A.6.3 Project Schedule

Activities for this WA will be performed from October 2012 to December 2013. The project schedule and main activities to be conducted are shown in Table A6.2. Monthly progress reports will be submitted by Pegasus and Shaw to the EPA WA Manager. At the conclusion of this study, an interim summary report will be submitted by the Pegasus Team to the EPA WA Manager. Two weeks after receiving comments from EPA, a final report on this study will be submitted to the EPA WA Manager.

Table A6.2 Project Schedule

	Oct 2012	Dec 2012	Feb 2013	Apr 2013	Jun 2013	Aug 2013	Oct 2013	Dec 2013	Jan 2014	Feb 2014
QAPP Preparation										
Field Sampling										
Experimental Tasks										
Sample Analysis										
Data Verification/Validation										
Monthly Reports										
Report Writing										
Report Submission										

A7 QUALITY OBJECTIVES AND CRITERIA

This is an EPA NRMRL Category I research project. In order to address the project objectives, generation of reliable data is vital. It is widely known that environmental samples are heterogeneous and variable even at micro-scale. Thus, the chances of controlling the variability in environmental samples will be difficult. Sample collection utilizing homogenization with equal proportion, maintaining at the same oxidation/reduction status, preservation (acidification, oxygen-free condition) and storage at cold conditions (at 4 ± 2 °C) can help minimize further variability. Additionally, the use of calibrated measuring and weight equipment, appropriate laboratory ware, unadulterated chemicals from the same vendor as well as maintaining quality control measures during sample analysis further strengthens the generation of reliable data. The QA/QC and verification criteria for the analytical methods used during this project are discussed in Section B.

A8 SPECIAL TRAINING/CERTIFICATION

All EPA personnel performing field sampling activities will complete the training required by the EPA Cincinnati Chemical Hygiene Plan. The Health and Safety Plan (HASP) on file also includes information on the project-specific safety training and requirements.

Within one week of endorsement of this QAPP by EPA, the WA Leader and Pegasus Contract QA Manager will provide training to the UC Team staff on the QAPP requirements. QAPP requirements training for EPA staff will be handled by the EPA PI or EPA WA Manager.

As required by the EPA ORD Policies and Procedures Manual, Section 13.4 *Quality Assurance/Quality Control Practices for ORD Laboratories Conducting Research*, analyst proficiency to perform sample analysis in accordance with an approved analytical method will be demonstrated and documented for Pegasus Team members assigned to perform sample analysis in support of this WA. The following must be completed by the analyst to demonstrate proficiency with the analytical method: 1) performing valid initial calibrations, 2) performing MDL determinations, 3) demonstrating that their results meet all minimum QA/QC acceptance criteria as presented in the method document, and if available, 4) satisfactorily analyzing a performance evaluation

sample or a second source standard. It is anticipated that performance evaluation samples will be submitted for all analytical methods that will be performed under this QAPP (i.e., TDS, acetic acid, TOC, ammonia-N, and nitrate-N measurements). PE samples are further discussed in Section C.

Safety training records for EPA and EPA on-site contractor staff are maintained by the EPA Safety, Health, and Environmental Management (SHEM) Office at EPA AWBERC. Training documentation for contract staff at UC will be maintained by the UC Manager, while the EPA PI will maintain the training documentation for EPA staff. Initial demonstration of analyst proficiency documentation for the UC staff are maintained by the UC Manager and reviewed by Pegasus Contract QA Manager. The EPA PI is responsible for data management, while purchasing documentation for PE samples and standards are maintained by the EPA WSWRD QA Manager, and the EPA WA Manager, respectively.

A9 DOCUMENTS AND RECORDS

Data collection efforts will not be initiated under this WA until this QAPP has been approved by EPA. Upon approval, an electronic copy of this QAPP will be prepared and identified as a controlled document by approval signatures on Section A1, Title Approval Sheet. The WA Leader will provide and/or make available the most current versions of this QAPP to all persons identified in Section A3, Distribution List. The WA Leader is responsible for ensuring that designated project personnel have the current version of the approved QAPP. Revisions and amendments to controlled WA documents (i.e., this QAPP and associated SOPs) will be reviewed and approved by the same process as the original. Persons identified in Section A3, Distribution List, will be advised by the WA Leader of the updates by E-mail memorandum, during staff meetings, or other appropriate method as determined by the needs of the project. Project staff will be responsible for destroying superseded versions of controlled documents upon notice.

Field and laboratory paper records will be maintained in accordance with Section 13.2, *Paper Laboratory Records*, of the EPA ORD Policies and Procedures Manual. The WA Leader will submit the raw data, including calculations and QA/QC requirements, electronically in Microsoft Excel format to the EPA WA Manager on a monthly basis. Monthly progress reports will be generated by the WA Leader, reviewed by the Pegasus On-Site Technical Manager and Project Manager, and submitted to EPA every month. Distribution of the monthly report to other agencies will be at the discretion of the EPA WA Manager. The expected product of this research will be at least one final report describing the analytical results of the samples analyzed. Records will be generated in both paper (hard copy) and electronic formats, and submitted in the format requested by the EPA WA Manager. The following original documents generated in support of WA activities constitute records which will be managed by the Pegasus Team:

- Contract-required documents and deliverables;
- WA-specific planning documents (i.e., Work Plan and this QAPP);
- Documentation that supports fulfillment of WA-specific planning document requirements, including QA assessment reports;

- Incoming WA-related correspondence from EPA;
- Outgoing WA-related correspondence to EPA.

Controlled access facilities that provide a suitable environment to minimize deterioration, tampering, damage, and loss will be used for the storage of records. Whenever possible, electronic records will be maintained on a secure network server that is backed up on a routine basis. Electronic records that are not maintained on a secure network server will be periodically backed up to a secure second source storage media, transferred to an archive media (e.g., compact discs, optical discs, magnetic tape, or equivalent), or printed. Electronic records that are to be transferred for retention will be transferred to an archive media or printed, as directed by EPA. Original records generated under this WA will be retained permanently. Active records will be stored at UC. Inactive records will be transferred from UC to EPA AWBERC for retention, unless otherwise directed by the EPA WA Manager.

SECTION B DATA GENERATION AND ACQUISITION

B1 SAMPLING PROCESS AND DESIGN

B1.1 Task 1

Throughout the project, the feeding flow rate and the mixed liquor pH will be monitored on a daily basis to ensure optimum conditions for biological activity (i.e., a pH value from 7 to 8). To assess microbial activity, TSS, and volatile suspended solids (VSS) will be measured twice a week (on Tuesday and Thursday) in the chemostats' mixed liquor. Additionally, the strength of the influent (acetic acid, TOC, ammonia [NH₃], and TDS) and effluent (acetic acid, TOC, NH₃, nitrate [NO₃], and TDS) will also be determined by grabbing samples on the same weekly schedule. In both chemostats (Figure A6.1), sampling ports for the mixed liquor and effluents are located on the lid and in the effluent line, respectively. Grab samples will be collected through these ports, previously purged (i.e., the first 30 mL will be wasted). The feed groups will be sampled separately. Hence, organics will be tested for TOC, while ammonia and acetic acid will be measured in the Nutrients reservoir. TDS will be determined in the buffer influent stream. Samples will be directly withdrawn from the corresponding lines, which will have quick disconnect-fittings. Again, these conduits will be purged by wasting the initial 30 mL. Influent and airflows as well as mixing conditions will not be stopped during sampling.

B1.2 Task 2

As stated in Section A6.1, WWTF samples will be collected by the EPA Project Scientist (Kit Daniels) under the supervision and guidance of the EPA WA Manager (Craig Patterson) and PI (Chris Impellitteri). The samples will be collected from three to five commercial treatment and reuse facilities that are located in the Marcellus Shale Region. WW sampling locations at the treatment facilities will be from sampling ports located on the WWTF influent (OGWW) and WWTF effluent (processed water) tanks.

The WWTF influent and WWTF effluent water will be collected into the sample containers after discarding the initial flow from sampling port for 30 seconds. In addition, the containers will be rinsed with the sample 2 times before sample collection. High density polyethylene (HDPE) amber carboys will be used for bulk OGWW sample collection. Due to challenges in sample procurement, every effort will be made to procure as much sample as possible (e.g., 160 L of WWTF effluent and 40 L of WWTF influent) for continuity in the study. Determining the concentrations of analytes/compounds at the time of field sample collection is not a study objective for this project. Field samples will not be pH adjusted or otherwise preserved at the time of collection. All samples will be transported or shipped in hard sided coolers under cold preservation using ice or ice packs.

During this task, two independent buffer reservoirs will be needed per chemostat (see Section A6.1). Actual OGWW will be fed onto Reactor 1 through one of buffer reservoirs at TDS values in multiples of 10 g/L, while the second carboy will be fortified with NaCl so that an equal TDS concentration is introduced in Reactor 2. For sampling purposes, a similar approach to that described for Task 1 will be followed, with TDS to be measured in the two buffer streams.

B2 SAMPLING METHODS

The monitoring parameters for Task 1 (Chemostats) and Task 2 OGWW are presented in Tables B2.1 through B2.3. This schedule will continue for the duration of the project unless some changes are recommended to obtain better representative data. After sampling the reactors, the analysis of the required parameters will be conducted immediately. If the analysis cannot be performed the same day for any parameter, the corresponding aliquot will be collected, preserved, and held in storage as described in Table B2.2 until analysis.

For field samples (Task 2), a one-time sampling event from each of the three to five treatment facility locations is planned for this study. It is anticipated that the samples will be collected from the treatment facility locations and transported back to EPA AWBERC on the same day, and then transferred to UC for processing and analysis. In the event that samples cannot be transported back to EPA AWBERC on the same day of collection, the samples will be shipped directly to the WA Leader (Pablo Campo) at UC via courier (e.g., Federal Express) the day of collection. The quantities of sample to be collected for each matrix/analysis, as shown in Table B2.3, reflect quantities needed to complete all tests for this study.

All water samples will be analyzed for NH₃, TOC, pH, NO₃, TDS, TSS, and VSS within one week of arrival at UC to obtain approximate background concentrations. In addition, all samples from each sampling location will be analyzed prior to starting each experiment to serve as control for that experiment. Since the samples were not preserved in the field, and since the analyses are not being conducted within their respective holding times, the analyses values will not be considered representative of field values at any time during this study. All analyses will be conducted at UC.

Table B2.1 Chemostat Sampling Strategy Summary

Sample/ Measurement Location	Matrix	Measurement	Frequency	Experimental QC	Total Number of Samples at each Sampling
Reactors 1 and 2	Influent	Flow rate	Daily	---	---
		TDS	Twice a week ¹	Triplicate	3
		Acetic acid	Twice a week ¹	Triplicate	4
		TOC	Twice a week ¹	Triplicate	3
		NH ₃	Twice a week ¹	Triplicate	4
	Effluent	Acetic acid	Twice a week ¹	Triplicate	4
		TOC	Twice a week ¹	Triplicate	3
		NH ₃	Twice a week ¹	Triplicate	4
		NO ₃	Twice a week ¹	Triplicate	4
		TDS	Twice a week ¹	Triplicate	3
	Mixed Liquor	pH	Daily	--	1
		TSS/VSS	Twice a week ¹	Triplicate	3

¹Sampling events to be conducted on Tuesday and Thursday. For acetic acid, TOC, NH₃ and NO₃, TOC, an additional aliquot of samples will be collected at the third sampling event of each 3 SRT period for matrix spikes; a %RSD will be calculated for the triplicates and percent recoveries will be calculated for the matrix spikes. The %RSD and spike recoveries have to meet the criteria listed in Table B5.1.

Table B2.2 Chemostat Experimental Sampling and Analytical Procedures to Be Used

Matrix	Measurement	Sampling/ Measurement Method	Analysis Method	Sample Container/ Quantity of each Sample to be analyzed	Preservation ¹ / Storage	Holding Time
Influent	Flow rate	---	Read volume change per unit time [Liter/Day]	---	None	N/A
	pH	Grab sample	Standard Method 4500-H B (see Appendix A)	40 mL glass vials /20 mL	None	Immediate analysis
	TOC	Grab sample	Standard Method 5310 B (see Appendix C)	40 mL glass vials /20 mL	H ₂ SO ₄ addition to pH 2/ Store @ 4±2 °C	28 d
	TDS	Grab sample	Standard Method 2540 D (see Appendix D)	40 mL glass vials /10 mL	Refrigeration/ Store @ 4 ± 2°C	7 d
	NH ₃	Grab sample	Standard Method 4500-NH ₃ D (see Appendix E)	40 mL glass vials /20 mL	H ₂ SO ₄ addition to pH 2/ Store @ 4±2°C	28 d
	Acetic Acid	Grab sample	Standard Method 5560D (see Appendix F)	40 mL glass vials /1 mL	Refrigeration/ Store @ 4 ± 2°C	7 d

¹Samples to be analyzed on sampling day do not require preservation, otherwise collect, preserve, and store subsamples as described.

Table B2.2 Chemostat Experimental Sampling and Analytical Procedures to Be Used (continuation)

Matrix	Measurement	Sampling/ Measureme nt Method	Analysis Method	Sample Container/ Quantity of each Sample to be analyzed	Preservation¹ / Storage	Holding Time
Effluent	TOC	Grab sample	Standard Method 5310B (see Appendix C)	40 mL glass vials/20 mL	H ₂ SO ₄ addition to pH 2/ Store @ 4 ± 2°C	28 d
	TDS	Grab sample	Standard Method 2540 D (see Appendix D)	40 mL glass vials/10 mL	Refrigeration/ Store @ 4 ± 2°C	7 d
	NH ₃	Grab sample	Standard Method 4500-NH ₃ D (see Appendix E)	40 mL glass vials/20 mL	H ₂ SO ₄ addition to pH 2/ Store @ 4 ± 2°C	28 d
	NO ₃	Grab sample	Standard Method 4500-NO ₃ B (see Appendix G)	40 mL glass vials/1 mL	H ₂ SO ₄ addition to pH 2/ Store @ 4 ± 2°C	28 d
	Acetic Acid	Grab sample	Standard Method 5560 D (see Appendix F)	40 mL glass vials/1 mL	Refrigeration/ Store @ 4 ± 2°C	7 d
Mixed Liquor	pH	Grab sample	Standard Method 4500-H B (see Appendix A)	40 mL glass vials/20 mL	None	Immediate analysis
	TSS/VSS	Grab sample	Standard Methods 2540 D and 2540 E (see Appendix B)	40 mL centrifuge tubes/10 mL	Refrigeration/ Store @ 4 ± 2°C	7 d

¹ Samples to be analyzed on sampling day do not require preservation, otherwise collect, preserve, and store aliquots as described.

Table B2.3 Field Sample Collection

Sample	Quantity of Field Sample collection	Sample Container	Preservation
WWTF Influent from Source 1	40 L	20 L carboy	4 ± 2 °C
WWTF Influent from Source 2	40 L	20 L carboy	4 ± 2 °C
WWTF Influent from Source 3	40 L	20 L carboy	4 ± 2 °C
WWTF Influent from Source 4 (if available)	40 L	20 L carboy	4 ± 2 °C
WWTF Influent from Source 5 (if available)	40 L	20 L carboy	4 ± 2 °C
WWTF Effluent from Source 1	160 L	20 L carboy	4 ± 2 °C
WWTF Effluent from Source 2	160 L	20 L carboy	4 ± 2 °C
WWTF Effluent from Source 3	160 L	20 L carboy	4 ± 2 °C
WWTF Effluent from Source 4 (if available)	160 L	20 L carboy	4 ± 2 °C
WWTF Effluent from Source 5 (if available)	160 L	20 L carboy	4 ± 2 °C

B3 SAMPLE HANDLING AND CUSTODY

Preservation of samples is required to retain integrity. The most common preservation techniques include pH adjustment and temperature control. Field personnel collecting environmental samples will store the samples at 4 ± 2 °C during shipment to the EPA. Table B2.3 provides the sample containers and the amount of sample to be collected from each water source. Except for temperature control, no other preservation techniques will be used for sample shipment from the field to UC.

A chain-of-custody (Appendix H) will be used to maintain a record of sample collection, transfer between personnel, shipment, analytical requests, and receipt by the laboratory. The following chain-of-custody procedures will be followed to guarantee sample custody documentation. A sample will be considered under proper custody if (1) it is in actual physical possession of the responsible person; (2) it is in view of the responsible person; (3) is locked in a container controlled by the person; or (4) has been placed into a designated secure area by the responsible person.

Field personnel who collect the samples are responsible for the care and custody of the samples until they are transferred or delivered to the delivery agent. A chain-of-custody form will accompany all samples. When transferring the samples, the individuals relinquishing and receiving the samples will sign, date, and note the time on the chain-of-custody form.

For Task 1, samples collected from the chemostat reactors will be labeled as shown in Table B3.1. All samples will be collected, stored, and analyzed at UC. No shipment of samples are planned for Task 1 activities.

For Task 2, the OGWW to be used in the study will be transported in hard-sided coolers from the field site on ice and padded with adequate packaging material to protect the samples from breaking during shipment. All containers used to collect the samples will be labeled. This label will contain the sample location, date and time of sampling. A laboratory notebook will be used by the field sampling team to record the details of the field sampling event. The samples will either be transported from the field site to UC, or shipped via courier directly to UC by the field sampling team. Samples will be transferred/shipped using coolers and packed with bagged ice or gel packs to maintain cold preservation storage. A chain-of-custody form (Appendix H) will be included with the samples. For samples shipped via courier, the relinquished chain-of-custody form will be placed in a Ziploc bag and taped to the inside lid of the cooler, and custody seals will be affixed to the lid/body of the cooler to provide evidence that samples were not tampered with during shipment.

Upon receipt at UC, samples will be refrigerated at 4 ± 2 °C prior to analysis. Samples will be thoroughly mixed via agitation prior to collection of sub-samples for analyses. Sample labeling will be maintained as mentioned above in accordance with the chain of custody information. A laboratory notebook will be used to record the details that will be signed, dated, and witnessed.

Table B3.1 Sample Identification Code

Position	Code
1	1 = Reactor 1 2 = Reactor 2
2-7	Date (mm/dd/yy)
8-9	Matrix I = Influent E = Effluent ML = Mixed Liquor
10-13	Test identifier TOC = Total Organic Carbon TDS = Total Dissolved solids NH ₃ = ammonia NO ₃ = Nitrate SS = Total/Volatile suspended solids HAc = Acetic Acid
14	Replicate 1, 2, or 3

B4 ANALYTICAL METHODS

The methods for analysis are summarized in Table B4.1. All chemicals involved in these analytical procedures are of ACS reagent grade or equivalent unless otherwise noted. Should any method call for modifications, the EPA WA Manager will be notified before modifications are made, and the changes will be documented as amendments to this QAPP.

Special attention should be paid to the analytical balance that will be used for the measure of TSS/VSS and TDS (see Table 4.1.); for its maintenance, calibration, and verification follow the guidelines included in Section 13.4 of the EPA ORD Policies and Procedures Manual and Table

B5.1. For the determination of VSS and TSS, it is very important to make sure that the Gooch crucibles and the 0.45 micron filters are prepared as herein described before the analysis of samples. Filters should be inserted in the crucibles and ignited at 450 °C for 1 hour and stored in a desiccator until needed. In the case of TDS, disposable inert aluminum weigh dishes will be used, which do not require pre-treatment before use.

Table B4.1. Outline of Analysis Methods

Analyses	Measurement	Instrument	Analytical Method
pH	Non-critical	Orion Model 720A pH meter	Standard Method 4500-H B (Appendix A)
TSS and VSS	Non-critical	0.45µm Glass fiber filters, 25 mL baking crucibles, 105 °C oven and 550 °C Muffle Oven, and Ohaus analytical plus balance AP2500	Standard Methods 2540 D and 2540 E (Appendix B)
TOC	Critical	TOC-V CSH Total Organic Carbon Analyzer, Shimadzu	Standard Method 5310B (Appendix C)
TDS	Critical	G4 Glass fiber filters, 180 °C oven, and Ohaus analytical plus balance AP2500	Standard Method 2540 D (Appendix D)
NO ₃	Non-critical	HP 8452 Diode Array spectrophotometer	Standard Method 4500-NO ₃ (Appendix G)
NH ₃	Non-critical	Thermo Orion model 720A pH/ISE meter; NH ₃ Ion-specific electrode probe	Standard Method 4500-NH ₃ D (Appendix E)
Acetic Acid	Non-critical	Agilent 6890 Series GC system equipped with a Flame Ionization Detector, 80/120 Carbopack B-DA/4% Carbowax Packed Column, Nitrogen 25 mL/min	Standard Method 5560D (Appendix F)

B5 QUALITY CONTROL

Instruments/equipment will be maintained in accordance with the EPA ORD Policies and Procedures Manual, Section 13.4, *Minimum Quality Assurance (QA)/Quality Control (QC) Practices for ORD Laboratories Conducting Research*, and in accordance with the analytical methods shown in Table B4.1. All analytical data will be collected in accordance with the QA/QC procedures specified in this QAPP. Table B5.1 summarizes the QA/QC checks, acceptance criteria, and corrective actions for each analysis. The data quality indicators for the analyses are defined in Sections B5.1 through B5.5.

B5.1 Precision

Precision is broadly defined as the scatter within any set of repeated measurements. For samples that are measured in duplicate, precision will be calculated as relative percent difference (RPD).

$$RPD = (C1 - C2) / ((C1 + C2) / 2) * 100 \quad (1)$$

where C1 and C2 are the two measurements. For samples that are measured in triplicate or higher, the precision will be measured as the relative standard deviation (RSD).

$$RSD = (S / SM) * 100 \quad (2)$$

where S is the standard deviation, and SM is the sample mean. Precision of the measurements

that cannot be calculated with Equations (1) and (2) will be determined by absolute range (AR).

$$AR = |C1 - C2| \quad (3)$$

where C1 and C2 are the two measurements.

B5.2 Accuracy

Accuracy is broadly defined as how close the analyses will come to the true concentration in the sample. The accuracy of measurements, incorporating a standard reference material or a second source standard, will be calculated as percent recovery.

$$\% \text{ Recovery} = 100\% * (Cs/Cmst) \quad (4)$$

where Cs is the measured concentration of the standard and Cmst is the actual concentration of the standard. The accuracy of the analyses that use matrix spikes will be calculated by

$$\% \text{ Recovery} = 100\% * (Csp - Cmsa) / Cac \quad (5)$$

where Csp is the measured concentration of the spiked aliquot, Cmsa is the measured concentration of the sample, and Cac is the actual concentration of the spiked aliquot.

The accuracy of the samples that cannot be determined with Equations (4) and (5) will be calculated by the measurement bias.

B5.3 Comparability

Data comparability will be maintained through the use of defined and consistent sampling and analytical procedures.

B5.4 Sensitivity

Sensitivity is the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest. The minimum concentration will be determined by the method, thus the MDL is implemented (EPA, 1986). MDLs for all analytes are calculated as outlined in CFR Title 40: Protection of the Environment Part 136-Guidelines establishing test procedures for the analysis of pollutants, Appendix B to Part 136-Definition and procedure for the determination of the Method Detection Limit-Revision 1.11.

The lowest calibration standard concentration will serve as the quantitation limit (QL), below which, all results will be reported as estimated value with a "J" qualifier. The QC acceptance criteria for the low-level calibration standard will be based on the criteria stated in each method. It should be noted that data will not be reported less than the lowest calibration standard without qualification.

Table B5.1 Summary of QA/QC Checks

Analysis/ Matrix/ (SOP)	Measurement	QA/QC Check	Frequency	Acceptance Criteria	Corrective Action
Analytical Balance Mass Measurements for TSS, VSS, and TDS Analysis	Critical	Calibration Check using two masses that bracket anticipated mass of the sample(s) to be measured	Daily prior to use	$\pm 0.01\%$ of mass true value	Zero balance, verify balance is level, and repeat balance calibration verification. If balance still fails, the balance may be calibration.
pH Mixed Liquor (Standard Method 4500 B)	Non-critical	Initial Calibration Calibration Verification	2 point calibration daily prior to use Run mid-point standard following initial calibration, after every 10 samples, and at end of batch	≤ 0.1 pH units	Recalibrate Recalibrate
TSS and VSS Mixed Liquor (Standard Methods 2540 D and 2540 E)	Non-critical	Initial crucible and filter weight check before analysis Analysis replicates	Repeat weight measurement for 2 crucibles per batch Triplicates every batch	Duplicate determination should agree within 5% of their average RSD < 20%	Prepare fresh crucible and filter Re-run affected samples if possible or qualify data if re-run not possible

Analysis/ Matrix/ (SOP)	Measurement	QA/QC Check	Frequency	Acceptance Criteria	Corrective Action
TOC Influent and Effluent (Standard Method 5310B)	Critical	Initial calibration with at least 5 points	Beginning of experiment or when the continuing calibration fails	According to calibration curve \pm 20% of target concentrations	Acceptable calibration curve must be generated prior to analyzing samples, prepare new standards and re-run until criteria met
		Laboratory Control Sample (LCS, second source)	Following calibration	\pm 20% of the true value	Recalibrate Instrument. Analysis cannot proceed without a passing LCS.
		Continuing calibration check	Beginning/end of each sequence and every 10 samples	\pm 20% recovery of mid-range standard	Re-run fresh standard, if fails, recalibrate and reanalyze all the affected samples
		Method blank	Beginning/end of each sequence and every 10 samples	TOC < 1/2 reporting level	Investigate and correct problem, if possible. Re-run affected samples if possible or qualify data if re-run not possible
		Lab Fortified Sample Matrix (LFSM)	Once at the 3 rd sampling event each 3 SRT period	Spike recoveries between \pm 20%	Re-run fresh LFSM, if fails, recalibrate and reanalyze all the affected samples
		Analysis replicates	Triplicates	RSD < 20%	Re-run affected samples if possible or qualify data if re-run not possible

Analysis/ Matrix/ (SOP)	Measurement	QA/QC Check	Frequency	Acceptance Criteria	Corrective Action
TDS Influent and Effluent (Standard Method 2540 D)	Critical	Initial aluminum dish weight check before analysis	Repeat weight measurement for 3 dishes per batch	Duplicate determination should agree within 5% of their average	Replace aluminum dish
		Analysis replicates	Triplicates every batch	RSD < 20%	Re-run affected samples if possible or qualify data if re-run not possible
		Accuracy check LFB containing NaCl 10 g/L	Every batch	± 20% recovery of NaCl target concentration	Re-run fresh LFB, if fails, Re-run affected samples
		Contamination check (lab blank)	One per batch	< 2 mg/L	Investigate the problem; reanalyze samples.

Analysis/ Matrix/ (SOP)	Measurement	QA/QC Check	Frequency	Acceptance Criteria	Corrective Action
NO₃ Effluent (Standard Method 4500- NO₃ B)	Non-critical	Initial calibration with at least 5 points	Beginning of experiment or when the continuing calibration fails	According to calibration curve \pm 20% of target concentrations	Acceptable calibration curve must be generated prior to analyzing samples, prepare new standards and re-run until criteria met
		Quality control sample (QCS) (second source)	One per batch following calibration	\pm 20% of the true value in a mid-range standard	Recalibrate Instrument. Analysis cannot proceed without a passing LCS.
		Continuing calibration check	Beginning/end of each sequence and every 10 samples	\pm 20% recovery of each analyte in a mid-range standard	Re-run fresh standard, if fails, recalibrate and reanalyze all the affected samples
		Method blank	Beginning/end of each sequence and every 10 samples	Absorbance < 1/5 of lowest calibration standard	Investigate and correct problem, if possible.
		Lab fortified sample matrix (LFSM)	Once at the 3 rd sampling event of each 3 SRT period	Spike recoveries between \pm 20%	Re-run fresh LFSM, if fails, recalibrate and reanalyze all the affected samples
		Analysis replicates	Triplicates	RSD < 20%	Re-run affected samples if possible or qualify data if re-run not possible

Analysis/ Matrix/ (SOP)	Measurement	QA/QC Check	Frequency	Acceptance Criteria	Corrective Action
NH₃ Influent and Effluent (Standard Method 4500- NH₃ D)	Non-critical	Initial calibration with at least 5 points	Every batch or when the continuing calibration fails	According to calibration curve \pm 20% of target concentrations	Acceptable calibration curve must be generated prior to analyzing samples, prepare new standards and re-run until criteria met
		Quality control sample (QCS) (second source)	One per batch following calibration	\pm 20% of the true value	Recalibrate Instrument. Analysis cannot proceed without a passing QCS.
		Continuing calibration check	Every 3 samples	\pm 20% recovery of each analyte in a mid-range standard	Re-run fresh standard, if fails, recalibrate and reanalyze all affected samples.
		Method blank	Beginning/end of each sequence and every 10 samples	<0.1 mg/L	Investigate and correct problem, if possible
		Lab fortified sample matrix (LFSM)	Once at the 3 rd sampling event of each 3 SRT period	Spike recoveries between \pm 20%	Re-run fresh LFSM, if fails, recalibrate and reanalyze all the affected samples
		Analysis replicates	Triplicates	RSD < 20%	Re-run affected samples if possible or qualify data if re-run not possible

Analysis/ Matrix/ (SOP)	Measurement	QA/QC Check	Frequency	Acceptance Criteria	Corrective Action
Acetic Acid Influent and Effluent (Standard Method 5560 D)	Non-Critical	Initial calibration with at least 5 points	Beginning of experiment or when the continuing calibration fails; fresh curve each month	According to calibration curve \pm 20% of target concentrations and $R^2 > 0.995$	Acceptable calibration curve must be generated prior to analyzing samples, prepare new standards and re-run until criteria met
		Initial calibration check (second source)	Following calibration	\pm 20% recovery of mid-range standard	Re-run fresh standard, if fails, recalibrate
		Continuing calibration check	Beginning/end of each sequence and every 10 samples	\pm 20% recovery of mid-range standard	Re-run fresh standard, if fails, recalibrate and reanalyze all the affected samples
		Method blank (reagent water adjusted to pH 2 with Pivalic Acid)	Beginning/end of each sequence and every 10 samples	Acetic acid < MDL	Investigate and correct problem, if possible. Re-run affected samples if possible or qualify data if re-run not possible
		Lab fortified sample matrix (LFSM)	Once at the 3 rd sampling event of each 3 SRT period	Spike recoveries between \pm 20%	Re-run fresh LFSM, if fails, recalibrate and reanalyze all the affected samples
		Analysis replicates	Triplicates	RSD < 20%	Re-run affected samples if possible or qualify data if re-run not possible

Table B5.2 Established MDL and QL for Parameters

Contaminants	MDL mg L ⁻¹	QL mg L ⁻¹
Acetic Acid	0.86	8.6
NO ₃	0.13	1.3
TOC	0.24	2.4

Note: All MDLs are based on calibration matrices and numbers are rounded to 4 decimals. For each analyte, the lowest calibration standard concentration will serve as the quantitation limit (QL), below which, all results will be reported as estimated value with a “J” qualifier. Actual MDLs and QLs will be included with the analytical reports for Acetic Acid, NO₃, and TOC.

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION AND MAINTENANCE

Testing, inspection and maintenance of equipment required for completion of analytical measurements will be conducted as needed to ensure proper operation. Generally, variability in known concentration of analytes will be used to test and inspect instrument. All records are to be kept by the individual responsible for the equipment. Maintenance will be performed by the manufacturer’s representative as needed.

B7 INSTRUMENT/EQUIPMENT CALIBRATION FREQUENCY

Instrument calibration is discussed in Table B5.1 and will be performed daily prior to each analysis.

B8 INSPECTION/ ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Supplies and consumables are listed in the attached method, and will be inspected upon receipt by the person that will be using the supplies and consumables. Acceptance of these will be based upon visually determining that received material is consistent with project requirements, packaging is intact or there is no obvious damage to the received materials. Items identified as damaged or contaminated will be declined.

B9 NON-DIRECT MEASUREMENTS

Non-direct data such as computer databases and programs will not be used in this study. However, during the final report preparation process study, results will be compared to reported data in the literature only where direct comparison is possible.

B10 DATA MANAGEMENT

As stated in Section A.9, laboratory paper and electronic records will be maintained in accordance with Section A.9. Data from each wet chemistry analysis will be recorded in a laboratory notebook or datasheet and each page will be dated and signed by the analyst who performs the analysis. Printed data from equipment runs will be filed separately in a three-ring binder(s) and labeled “WA-2-64” with the name of the analyte, year and the month. Raw data will be kept as hard copies and

computer files. Raw data from chemical instrumentation will be retained as required by EPA Record Schedules 501 and 507 and will be backed up onto a separate external hard drive.

If analytical instrumentation software/hardware allows for data export, raw instrument data will be automatically entered to Microsoft Excel spreadsheets. Microsoft Excel spreadsheets used for calculations and statistical analyses will be initially verified for accuracy by the analyst and then sent to a second reviewer. For manually entered data, transcription will also be checked initially for errors by the analyst and then sent to a second reviewer for review. Final data will be expressed in units shown in Table B10.1.

Table B10.1 Reporting Units

Measurement	Unit
Flow Rate	liters/day
pH	pH units
TSS/VSS	mg/L
NO ₃ -N	mg/L as N
TDS	mg/L
TOC	mg/L
NH ₃ -N	mg/L as N
Acetic acid	mg/L

SECTION C ASSESMENT AND OVERSIGHT

C1 EPA ASSESSMENTS AND RESPONSE ACTIONS

EPA will conduct readiness reviews, Technical Systems Audits (TSAs), Audits of Data Quality (ADQs), and Performance Evaluations (PEs). Readiness reviews will be conducted prior to the collection of any field samples to ensure that all personnel, training, equipment, supplies, and procedures are available and acceptable for environmental data to be collected in accordance with the governing QAPP. Acceptability or issues that were identified during readiness reviews will be communicated to the PI and EPA WA Manager via email. TSAs and PEs will be conducted early in the project to allow for identification and correction of any issues that may affect data quality. TSAs will be conducted only on laboratory activities since only bulk samples are collected in the field. Laboratory TSAs will focus on the critical target analytes. Detailed checklists, based on the procedures and requirements specified in this QAPP, related SOPs, and EPA Methods will be prepared and used during these TSAs. These audits will be conducted by the EPA/NRMRL HF QA Management Team or by QA support contractors with oversight by the QA Management Team.

ADQs will be conducted on a representative sample of data for the critical target analytes. These audits will be conducted by the EPA/NRMRL HF QA Management Team or by QA support contractors with oversight by the QA Management Team. See Section D1 for additional discussion on ADQs.

PEs will be conducted on target analytes (shown in Table A6.1) for those that are available commercially such as those from ERA, A Waters Company (Golden, CO). As part of the readiness review, PE samples must pass acceptably (as applicable) before any analysis can be done on project samples.

Assessors do not have stop work authority; however, they can advise the EPA WA Manager if a stop work order is needed in situations where data quality may be significantly impacted, or for safety reasons. The PI makes the final determination as to whether or not to issue a stop work order.

For TSA and ADQ reports that identify deficiencies requiring corrective action, the audited party must provide a written response to each Finding and Observation to the PI, which shall include a plan for corrective action and a schedule. (If the audited party is a contractor, then the response shall be delivered to the EPA WA Manager who will ensure delivery to the PI.) The PI is responsible for ensuring that audit findings are resolved. The QA Management Team will review the written responses to determine their appropriateness. If the audited party is other than the PI, then the PI shall also review and concur with the corrective actions. The QA Management Team will track implementation and completion of corrective actions. After all corrective actions have been implemented and confirmed to be completed; the QA Management Team shall send documentation to the PI and his supervisor that the audit is closed. Audit reports and responses shall be maintained by the PI in the project file and the QA Management Team in the QA files, including QLOG.

C1.1 Assessments

Detailed checklists are based on the procedures and requirements. The laboratory audit will take place when samples are in the laboratory's possession and in the process of being analyzed.

Laboratory TSAs will focus on the critical target analytes and will be conducted on-site at UC laboratories run by Pegasus Team contractors. It is anticipated this will take place immediately following the first sampling event.

ADQs will be conducted on a representative sample of data for the critical target analytes. These will be conducted on the first data packages to ensure there are no issues with the data and to allow for appropriate corrective actions on subsequent data sets if needed.

C1.2 Assessment Results and Reports

At the conclusion of a TSA, a debriefing shall be held between the auditor and the PI or audited party to discuss the assessment results. TSA and ADQ results will be documented in reports to the PI, the PI's first-line manager, and the WSWRD HF QA Manager and the ETAV QA Manager. If any serious problems are identified that require immediate action, the QA Management Team will verbally convey these problems at the time of the audit to the PI or audited party.

The PI is responsible for responding to the reports as well ensuring that corrective actions are implemented in a timely manner to ensure that quality impacts to project results are minimal.

C2 PEGASUS ASSESSMENTS AND RESPONSE ACTIONS

The Pegasus Contract QA Manager will conduct assessments of WA 2-64 to verify compliance with the requirements of this QAPP. Assessment activities include Technical System Assessments (TSAs), readiness reviews, and surveillances.

The three types of WA assessments are discussed below.

A Readiness Review will be conducted prior to the initiation of a WA, either by the Pegasus Contract QA Manager or by EPA). The Readiness Review is initiated to ensure that all personnel, training, equipment, supplies, and procedures are available for environmental data to be collected in accordance with the governing QAPP.

TSAs are thorough, systematic, and qualitative assessments of overall implementation of requirements in accordance with the WA QAPP and related quality documents. The TSA may include assessment of field sampling, laboratory operations, equipment, procedures, records management, or technology application in support of environmental data operations.

Surveillances will be incorporated into the assessment program to provide a less formal independent evaluation of items, activities, or processes for conformance with specific requirements. Performance areas that may be reviewed during surveillances include:

- Training and qualification of personnel

- SOPs
- Work performance
- Verification activities
- Documents and records
- Purchased items and services
- Measuring and test equipment.

The minimum QA/QC practices for ORD Laboratories, as discussed in Subsection 2.1.5, will be included in the periodic surveillance review cycle and assessed during scheduled laboratory surveillances. EPA, at their discretion, may also conduct assessments to verify compliance with the requirements of this QAPP.

Assessment activities that will be conducted by EPA include the submittal of PE samples (including double blind PE samples), readiness reviews, TSAs and ADQs (as described in Section C1). The Pegasus Team will fully cooperate with EPA for EPA-conducted assessments.

C2.1 Performance Evaluation (PE) Samples

If PE standards are available for the evaluation of the analytical methods described in this QAPP, Pegasus Team staff will analyze PE materials as directed by the EPA. The EPA WSWRD QA Manager may also choose to submit PE standards for analysis as an independent assessment of performance for a particular analytical method. All documentation, including sample receipt and storage, raw data, verification and validation of results, are included in the project file, as appropriate.

C2.2 Assessments

The Pegasus Contract QA Manager will conduct project assessments (i.e., TSAs, readiness reviews or surveillances) on a quarterly basis. Assessments will be conducted in accordance with Section 9 of the Pegasus QMP. The data may also be assessed by use of a laboratory-focused TSA as detailed in the WA Quality document. The TSA focuses on sample receipt and handling, method parameters, equipment maintenance and calibration, and/or data reduction requirements as specified in the WA Quality document.

C2.3 Corrective Actions

Deficiencies requiring corrective action will be documented on a Corrective Action Plan form by the responsible individual, as determined by the Pegasus On-Site Technical Manager, and submitted to the Pegasus Contract QA Manager. Corrective actions will be implemented by the individual(s) identified on the Corrective Action Plan form. The Pegasus Contract QA Manager will track corrective actions to closure and notify management when closure of items is complete.

C2.4 Reports to Management

Assessment reports will contain the assessment ID; location; purpose and scope; assessment type; assessment date(s); persons contacted; activities observed; and assessment results.

Assessment reports are prepared by the Pegasus Contract QA Manager and distributed to the WA Leader and Pegasus On-Site Technical Manager. A response is prepared for QA assessment findings by the WA Leader to the Pegasus Contract QA Manager within 30 days, unless otherwise specified, after receipt of the final assessment report. Corrective Action Plans are generated in response to assessment findings, logged and tracked by the Pegasus Contract QA Manager through closure. When all findings of the assessment have been closed, notice is sent by the Pegasus Contract QA Manager to the WA Leader and responsible manager.

SECTION D DATA VALIDATION AND USABILITY

D1 EPA DATA REVIEW REPORTS AND VALIDATION

Criteria that will be used to accept, reject, or qualify data will include specifications presented in this QAPP, including the methods used and the measurement performance criteria presented in Table B.5.1. In addition, sample preservation and holding times will be evaluated against requirements provided in Table B.2.1.

Data will not be released outside of NRMRL until all study data have been reviewed, verified and validated as described in this QAPP. The PI is responsible for deciding when project data can be shared with interested stakeholders in conjunction with the WSWRD Director's approval.

Data verification will evaluate data at the data set level for completeness, correctness, and conformance with the method. Data verification will be done by those generating the data. This will begin with the personnel in the field and the analysts in the laboratory, monitoring the results in real-time or near real-time. The contractor laboratories shall contact the PI upon detection of any data quality issues which significantly affect sample data. They shall also report any issues identified in the data report, corrective actions, and their determination of impact on data quality.

Data reports are reviewed by the PI for completeness, correctness, and conformance with QAPP requirements. All sample results are verified by the PI to ensure they meet project requirements as defined in the QAPP and any data not meeting these requirements are appropriately qualified in the data summary prepared by the PI (or in the work assignment deliverables prepared by contractors that will be used by the PI). See Section D3 for the Data Qualifiers. The Contract Laboratory Program guidelines on organic (EPA, 2008) and inorganic (EPA, 2010) methods data review are used as guidance in application of data qualifiers.

Data validation is an analyte- and sample-specific process that evaluates the data against the project specifications as presented in the QAPP. Data validation (i.e., audit of data quality) will be performed by a party independent of the data collection activity. Data summaries for the critical analytes that have been prepared by the PI as well as laboratory data reports and raw data shall be provided to the QAM, who will coordinate the data validation. The validation team shall evaluate data against the QAPP specifications. NRMRL SOP #LSAS-QA-02-0, "Performing Audits of Data Quality" will be used as a guide for conducting the data validation. The outputs from this process will include the validated data and the data validation report (ADQ Report). The report will include a summary of any identified deficiencies, and a discussion on each individual deficiency and any effect on data quality and recommended corrective action.

D2 PEGASUS TEAM DATA REVIEW, VERIFICATION, AND VALIDATION

Data verification and validation is performed following the guidance provided in the EPA guidance document entitled, *Guidance on Environmental Data Verification and Validation*, EPA QA/G-8.

Initial data assessment is conducted by an analyst who is knowledgeable regarding the WA Quality requirements. The analyst determines that samples have been analyzed, calibration and QC data requirements have been met, and the data are ready for verification. This assessment is documented on the data summary sheet.

A complete verification (100% of the data) is conducted by knowledgeable personnel other than the analyst, as assigned by the WA Leader, Pegasus Contract QA Manager, or On-Site Technical Manager. This verification is documented on the cover of the data summary. Data verification includes review of the data for completeness, correctness, and technical compliance as summarized below.

- Completeness
 - The data package received contains the documentation listed in the data validation section (below).
 - Forms and other required information have been completed.
 - All expected samples and analyses were reported.
 - Relevant information for each analysis, including QC results and supporting documentation, are included in the data package.
- Correctness
 - Results have been transcribed correctly to the reporting sheets.
 - Correct application of dilution factors.
 - Sample results are supported by valid QC.
 - Missing results and QC outliers have been noted.
- Technical compliance
 - Sample hold times were met.
 - The correct analytical method was used for each analysis, as specified in the QAPP.
 - The samples were properly preserved in accordance with the requested method.
 - Calculations, QC frequencies, and acceptance criteria applied to the data are the same as those specified in this QAPP.

Data validation of 10 percent of analytical data generated is conducted by qualified individuals (or organizations) that are sufficiently independent of those who performed the work, but are collectively equivalent in technical expertise. Data validation is conducted to ensure that activities are technically adequate, competently performed, properly documented, and satisfy established technical and quality requirements. The Pegasus Contract QA Manager is responsible for ensuring that assigned data validators are sufficiently independent to perform the validation.

Data validation tasks begin with a review of the QAPP requirements. The data are submitted to the validator in "packets." Each packet contains the data for one sampling event and the following information in the order given here (unless a different submittal packet is agreed to by the validator and the submitter):

- General overview of the data, including information such as the number of samples, the matrix, a brief background on the site and/or system from which the samples originated, and any known problems with the data in general or with specific samples. An example Laboratory Data Summary Report is provided in Appendix I.
- Field, chain-of-custody, or other pre-analysis information
- Standards data
- Initial calibration data
- Continuing calibration data
- Blank data
- Sample results, including raw data
- QC data.

Additional validation may be recommended if significant anomalies are detected during the 10 percent review. Significant anomalies may include missed holding times, calibration inconsistent with method and/or WA requirements, contaminated blank results, laboratory control samples outside control limits, replicate analysis outside RPD limits, matrix spike/matrix spike duplicate (MS/MSD) results outside recovery limits, or calculation errors.

D3 DATA QUALIFICATION

Data qualification is an integral component of data reporting, review and validation. During data reporting and review, qualifiers are applied to ensure the laboratory has provided data of known quality. During data validation, qualifiers are applied to alert the data end user to quality problems that may impact the usability of the data. Data qualifiers may be assigned to particular sample results based on available information, including: laboratory QC summaries, exceeded holding times, unavoidable analytical interference, laboratory data summary information, etc. The data qualifiers and other data descriptors to be used in this project are below in Table D3.1 and D3.2.

Table D3.1 Data Qualifiers

Qualifier	Definitions
U	The analyte was analyzed for, but not detected above the reported sample quantitation limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
J+	The result is an estimated quantity, but the result may be biased high.
J-	For both detected and non-detected results, the result is estimated but may be biased low.
B	The analyte is found in a blank sample above the quantitation limit, and the concentration in the sample is less than 10 times the concentration found in the blank.
H	The sample was prepared or analyzed beyond the specified holding time. Sample results may be biased low.
*	Relative percent difference of a field or lab duplicate is outside acceptance criteria.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be confirmed.

Table D3.2 Data Descriptors

Descriptor	Definitions
NA	Not Applicable (See QAPP)
NR	Not Reported by Laboratory or Field Sampling Team
ND	Not Detected
NS	Not Sampled

Application Notes for Data Qualifiers:

- If the analyte concentration was less than the Quantitation Limit (<QL), then the B qualifier will not be applied.
- If both an analyte and an associated blank concentration are between the MDL and QL, then the sample results are reported as <QL and qualified with U.
- For samples associated with high Matrix Spike recoveries, the J+ qualifier will not be applied if the analyte is less than the Quantitation Limit (<QL).

D4 RECONCILIATION WITH USER REQUIREMENTS

The data will be evaluated to check if they conform to the QA objectives of the project. A statistical assessment for accuracy, precision, and completeness will be performed. All analyses will be required to meet data quality objectives before formulation of the final report. The individual EPA Method or SOPs documenting an analysis will include a discussion of data











verification, including ascertaining matrix effects and instrumental biases. Where failures are observed in the individual methods, data will be marked as suspect.

Characterization sample data will be presented in tabular format or in figure. All parameters will be reported along with the mean, standard deviation and range, when applicable. Tabular data summaries will be included in the main discussion of the reports.

REFERENCES

U.S. Environmental Protection Agency, 2002. *Guidance on Environmental Data Verification and Validation*, EPA QA/G-8, EPA/240/R-02/004. Office of Environmental Information, Washington, DC.

APPENDICES

APPENDIX A	pH, Standard Method 4500-H B	 Appendix A - SM 4500-H B
APPENDIX B	Total and Volatile Suspended Solids, Standard Methods 2540 D and 2540 E	 Appendix B - SM 2540D  Appendix B - SM 2540E
APPENDIX C	Total Organic Carbon Standard Method 5310B	 Appendix C - SM 5310B
APPENDIX D	Total Dissolved Solids, Standard Method 2540 D	 Appendix D - SM 2540D
APPENDIX E	Analysis of Ammonia by NH ₃ Ion-specific electrode probe, Standard Method 4500-NH ₃ D	 Appendix E - SM 4500-NH3 D
APPENDIX F	VFAs ANALYSIS BY GC/FID, Standard Method 5560D	 Appendix F - SM 5560D
APPENDIX G	Analysis of NO ₃ by UV Spectrophotometric method, Standard Method 4500-NO ₃ A	 Appendix G - SM 4500-NO3 B
APPENDIX H	EPA Chain of Custody Form	 Appendix H - EPA Chain of Custody For
APPENDIX I	Example Laboratory Data Report	 Appendix I - Laboratory Data Rep